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“Nonlinear Ultrafast Spectroscopy of Electron and Energy Transfer in Molecule Complexes”

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This research program had resulted in 18 publications listed at the end of the report:

Density Matrix Analysis and Simulation of Electronic Excitations in Conjugated and Aggregated Molecules

An ab-initio density matrix algorithm for electronic structure computations of molecules and aggregates was developed. The reduced single-electron density matrices were derived by mapping the Density Functional Theory (TDDFT) nonlinear optical response functions onto an effective multilevel system. These density matrices were then used as a zero'th order iteration into self-consistent equations whose solution should yield the exact energies and the complete set of (transition and diagonal) single electron density matrices. Higher order (n electron) density matrices were not obtained explicitly. This method provides the linear and nonlinear optical response functions at a low computational cost. Applications were made to constructing an exciton Hamiltonian for molecular aggregates using density matrices of isolated molecules, avoiding electronic structure calculations of the entire aggregate.

Size scaling of intramolecular charge transfer driven optical properties of substituted polyenes and polyynes was investigated using this approach. The origin of dramatic variation in optical polarizabilities of push-pull conjugated chains with respect to the conjugation length was discussed. Ab initio calculations of intramolecular charge transfer (ICT)-driven dipole moment (μ_{CT}), polarizability (α_{CT}), and first hyperpolarizability (β_{CT}) show that the values of α_{CT} / μ_{CT} and β_{CT} / μ_{CT} change linearly and quadratically with respect to the conjugation length, respectively. The maximum ICT-driven coherence sizes of α_{CT} and β_{CT} were consistent with the time-dependent densities to the first ($\rho^{(1)}$) and second ($\rho^{(2)}$) orders of the electric field obtained from the collective electronic oscillators method.

Excited-State Molecular Dynamics Simulations of Conjugated Oligomers were carried out using the Electronic Density Matrix. Vibrational motions in optically excited polyacetylene and polydiacetylene oligomers were calculated using potential surfaces obtained from the collective electronic oscillators (CEO) technique. The role of the effective conjugation coordinate (ECC) in the relaxation processes following an impulsive vertical excitation from the ground state is demonstrated. Real-space analysis of the electronic transition density matrices shows the charge and bond-order redistribution taking place upon photoexcitation.

Nonlinear Spectroscopy of conjugated dendrimers

The doorway-window representation of sequential four wave mixing was combined with the nonlinear exciton equations (NEE) to calculate femtosecond pump probe spectra of the dendrimeric nanostar. The results were compared to previous time resolved fluorescence calculations. In addition to the signatures of single-exciton energy funneling from the periphery towards the center, the pump-probe signal also carries useful information about two exciton states. Direct signatures of exciton energy migration and the two-exciton states were identified. The frequency-domain pump probe signal shows the effects of exciton coupling and excited-state absorption. Further information obtained from different polarization configurations of the pulses was analyzed. Disorder effects on exciton migration in dendrimers were investigated. The center-bound excitonic diffusion on dendrimers subjected to several types of nonhomogeneous funneling potentials was considered. We first studied the mean first passage time MFPT for diffusion in a linear potential with different types of correlated and uncorrelated random perturbations. Increasing the funneling force, there was a transition from a phase in which the MFPT grows exponentially with the number of generations g to one in which it does so linearly. Overall the disorder slows down the diffusion, but the effect was much more pronounced in the exponential compared to the linear phase. When the disorder gives rise to uncorrelated random forces there was, in addition, a transition as the temperature T is lowered. This was a transition from a high- T regime in which all paths contribute to the MFPT to a low- T regime in which only a few of them do. We further explored the funneling within a realistic nonlinear potential for extended dendrimers in which the dependence of the lowest excitonic energy level on the segment length was derived using the time-dependent Hartree-Fock approximation. Under this potential the MFPT grows initially linearly with g but crosses over, beyond a molecular-specific and T -dependent optimal size, to an exponential increase. We further considered geometrical disorder in the form of a small concentration of long connections as in the *small world* model. Beyond a critical concentration of connections the MFPT decreases significantly and it changes to a power law or to a logarithmic scaling with g , depending on the strength of the funneling force.

One-dimensional Transport with Dynamic Disorder:

The mean quenching time distribution and its moments in a one-dimensional N -site donor-bridge-acceptor system were calculated. All sites were coupled to a two-state jump bath for arbitrary disorder and an arbitrary ratio of the bath jump rate and the average hopping rate. The quenching time distribution has long power-law tails even when

the waiting times are exponentially distributed. These disappear for fast fluctuations where the hopping rate self-averages on the bath relaxation time scale. In the absence of disorder, the mean quenching time scales linearly with N . Otherwise, we observe a power law with a crossover to linear scaling for large N . Distributions of particle position, its second moment, velocity and diffusion coefficient are computed in the infinite N limit. For longer times, the dynamic disorder self-averages and the average position, velocity, and diffusion coefficient scale linearly in time.

Three-Dimensional Nonlinear Optical Chromophores Based on Through-Space Delocalization:

Six permutations of 4-fold donor and/or acceptor substitution of paracyclophane at the various positions were synthesized to probe the phenomenon of three-dimensional delocalization on the nonlinear optical properties of organic materials. The interplay between through-bond intramolecular charge transfer (ICT) as well as three-dimensional, or through-space, ICT processes gives rise to large quadratic hyperpolarizability values. The determination of dipolar and octupolar irreducible tensor contributions to the overall $\chi^{(2)}$ tensor value was made possible by the polarized harmonic light scattering technique. The electric field-induced second-harmonic generation technique was also used for comparison. Significant experimental values for members of the series made of two centrosymmetric benzene-like units were a clear signature of a purely through-space ICT between two aryl subunits. The two configurational isomers that pair two dipolar donor-acceptor chromophores also exhibit octupolar character. Analysis of these two with an additive model revealed a strong three dimensional inter-ring charge transfer. Photophysical studies of pseudo-*p*-distyryl[2.2]paracyclophane, a model molecule of a stilbene dimer arranged in a brick-wall geometry, in tetrahydrofuran solution indicate the existence of at least two conformers in the ground state. The conformer **A** with the smallest optical gap of 3 eV has a short radiative lifetime of 3.3 ns, while the conformer **B** with an optical gap about 0.3 eV larger is much more abundant in solution and its radiative lifetime is about 10 times longer. Ab initio calculations show that the ground-state energy has a shallow minimum with respect to the torsional angle between the styryl side group and the paracyclophane core around the zero position, with the lowest energy conformation at a torsional angle of -21° . On this basis, were assigned to flat and twisted conformations, respectively. **B** shows a partial decay of excited-state absorption and fluorescence with a time constant ranging from 5 to 30 ps, depending on excitation photon energy. We attributed this to isomerization of the stilbene moiety, which initially keeps conjugation in the ground state. The isomerization product is long-lived and tends to accumulate in solution.

Probing single molecule kinetics by photon arrival trajectories:

Multitime correlation functions of photon arrival times in single molecule fluorescence resonant energy transfer measurements were computed using a simple model representing slow conformational dynamics described by a collective stochastic Gaussian coordinate. The analogy with time domain nonlinear optical spectroscopy was explored. Various statistical measures of distributions of single photon arrival times and fluorescence lifetimes were employed to analyze non-Poissonian statistics. Single photon counting-time distributions obtained from

single molecule photon arrival trajectories were employed in the theoretical study of multistate kinetics coupled to a two-state jump bath. The bath time scale has been extracted from statistical analysis of one- and two-point time-domain optical measurements. The amplitude and shape of the distribution of interphoton arrival times reflects bath correlations. A slow bath ~relative to the kinetics results in broad distributions of arrival times reflecting bath memory. For a fast bath, the arrival time distributions narrow around shorter times, similar to motional narrowing in frequency domain spectroscopy. The variance of either kinetic rates or equilibrium population of bath states results in asymmetry of the distribution of two photon arrival times.

A Mechanical Force Accompanies FRET

The coupling responsible for fluorescence resonance energy transfer (FRET) was shown to generate a mechanical force that is distinct from the van der Waals force between ground-state molecules and can be either attractive or repulsive. The underlying potential has the same $1/r^6$ distance dependence as the rate of FRET, and the two are connected by a Kramers-Kronig relation. Just as the rate of FRET can be derived either classically or quantum mechanically, so too can the interaction potential. Because of the FRET force, time-resolved FRET measurements contain information on the mechanical stiffness of the matrix containing donor and acceptor.

Multipoint Fluorescence Quenching Time Statics for Single Molecules with Anomalous Diffusion:

Three-point fluorescence lifetime correlation functions were computed for the fluorescence resonance energy transfer (FRET) and electron transfer (ET) quenching mechanisms in a single donor-acceptor system of which the distance X undergoes anomalous diffusion in a harmonic potential with short-time variance scaling as $\sim t^\alpha$. The three-point joint probability distribution of X and its moments are calculated by solving the fractional Fokker-Planck equation (FFPE). For $\alpha=1$, the process is stationary and the two- and three-point joint probability distribution was centered around the time-dependent average donor-acceptor separation, $\langle X(t) \rangle$. For $\alpha < 1$, the distribution slows down, becomes nonstationary, and remains centered at initial separation $X(0)$ even for times exceeding the bath correlation time scale.

Probing exciton dynamics using Raman resonances in femtosecond x-ray four-wave mixing:

Time-resolved coherent x-ray Raman signals of molecules were computed by formulating the nonlinear response in terms of correlation functions of charge and current densities. Simulations performed on one dimensional molecular chains demonstrate that Raman resonances provide a direct local probe for valence excitation dynamics with high spatial and temporal resolutions.

Nonlinear Response of Classical Dynamical Systems to Short Pulses:

Valuable insight into the nonlinear dynamics of a system can be gleaned from its response to a single intense short pulse. We derived expressions for the corresponding nonlinear response functions and show that the fluctuation-dissipation theorem may be extended beyond the linear response limit to an arbitrary pulse intensity. As an

illustrative example, we calculated response functions up to 11th order for the regular Lorentz gas in two dimensions.

Ultrafast Nonlinear Spectroscopic Techniques in the Gas Phase and Their Density Matrix Representation:

The possible time-resolved three pulse nonlinear spectroscopic techniques and their application to gas-phase samples were surveyed. The role of each of the interacting electric fields is specified, and the nature of the signal was interpreted using the density matrix representation. Simulations of these nonlinear optical signals were based on the perturbative solution of the Liouville equation for the density matrix to third order in the applied fields. Closed expressions were presented for the integrated and frequency dispersed signals that identify the type of molecular response for each technique and give the signal dependence on the various time delays between laser pulses. We choose a simple experimental system, two-electronic states coupled to a single vibrational mode of diatomic iodine, with weak dephasing, was chosen to illustrate various molecular polarization responses in fourwave mixing experiments including pump-probe, reverse transient grating, and photon echo. These signals and their simulations illustrated how the time delays between pulses can be effectively used to control the optical response of the molecular system.

Publications Resulting from the Grant

1. "Ultrafast Nonlinear Spectroscopic Techniques in the Gas Phase and Their Density Matrix Representation," B. I. Grimberg, V. V. Lozovoy, M. Dantus and S. Mukamel, *J. Phys. Chem A.*, **106**, 697-718 (2002).
2. "Excited State Molecular Dynamics Simulations of Conjugated Oligomers Using The Electronic Density Matrix," M. Tommasini, G. Zerbi, V. Chernyak and S. Mukamel, *J. Phys. Chem.* **105**, 7057-7071 (2001).
3. "Density Matrix Analysis and Simulation of Electronic Excitations in Conjugated and Aggregated Molecules," S. Tretiak, S. Mukamel, *Chem. Rev.* **102**, 3171-3212 (2002).
4. "Disorder and Funneling Effects on Exciton Migration in Tree-Like Dendrimers," S. Raychaudhuri, Y. Shapir and S. Mukamel, *Phys. Rev. E* **65**, 021803 (2002).
5. "Self-Consistent Density Matrix Algorithm for Electronic Structure and Excitations of Molecules and Aggregates," S. Mukamel and O. Berman, *J. Chem. Phys.*, **119**, 12194-12204 (2003).
6. "Femtosecond Pump-Probe Spectroscopy of the Dendrimeric Nanostar," A. Tortschanoff, A. Piryatinski, and S. Mukamel, *J. Lum.* **94-95**, 569-273 (2001).

7. "Pump-probe Simulation Study of the Two-Exciton Manifold of Dendrimers," A. Tortschanoff and S. Mukamel, *J. Phys. Chem B.* **106**, 7521-7529 (2002).
8. "Probing Single Molecule Kinetics by Photon Arrival Trajectories," V. Barsegov and S. Mukamel, *J. Chem. Phys.* **116**, 9802-9811 (2002).
9. "Conformations and Photophysics of Stilbene Dimer" A. Ruseckas, E.B. Namdas, J.Y. Lee, S. Mukamel, S. Wang, G. Bazan and V. Sundstrom, *J. Phys. Chem. A.* **107**, 8029-8034 (2003).
10. "Three Dimensional Non Linear Optical Chromophores Based on Through-Space Delocalization" G.P. Bartholomew, I. Ledoux, S. Mukamel, G.C. Bazan and J. Zyss, *J. Am. Chem. Soc.*, **124**, 13480-13485 (2002).
11. "Multidimensional Spectroscopic Probes of Single Molecule Fluctuations", V. Barsegov and S. Mukamel, *J. Chem. Phys.* **117**, 9465-9477 (2002).
12. "Size Scaling of Intramolecular Charge Transfer Driven Optical Properties of Substituted Polyenes and Polyynes", J.Y. Lee, B.J. Mhin, S. Mukamel, and K. S. Kim *J. Chem. Phys.* **119**(14) 7519-7524 (2003).
13. "Probing Exciton Dynamics Using Raman Resonances in Femtosecond X-Ray Four Wave Mixing" S. Tanaka and S. Mukamel, *Phys. Rev. A.* **67**, 033818 (2003).
14. "A Mechanical Force Accompanies FRET" A. Cohen and S. Mukamel, *J. Phys Chem. B.*, **107**, 3633-3638 (2003).
15. "The Role of Water on Electron-Initiated Processes and Radical Chemistry: Issues and Scientific Advances", B.C. Garrett, et.al, *Chem. Rev.* **105**, 355-389 (2005).
16. "Nonlinear Response of Classical Dynamical Systems to Short Pulses", C. Dellago and S. Mukamel, *Bull. Kor. Chem. Soc.* **24**, 1097-1101 (2003).
17. "One-dimensional Transport with Dynamic Disorder" V. Barsegov, Y. Shapir and S. Mukamel, *Phys. Rev. E.* **68**, 011101 (2003).
18. "Multipoint Fluorescence Quenching Time Statistics for Single Molecules with Anomalous Diffusion", V. Barsegov and S. Mukamel, *J. Phys. Chem.*, **108**, 15-24 (2004).